

EQUATION OF STATE AND HUGONIOT LOCUS FOR POROUS MATERIALS: P - α MODEL REVISITED

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Abstract. Foams, porous solids and granular materials have a characteristic Hugoniot locus that for weak shocks is concave in the (particle velocity, shock velocity)-plane. An equation of state (EOS) that has this property can be constructed implicitly from a Helmholtz free energy of the form $\Psi(V, T, \phi) = \Psi_s(V, T) + B(\phi)$ where the equilibrium volume fraction ϕ_{eq} is determined by minimizing Ψ , *i.e.*, the condition $\partial_\phi \Psi = 0$. For many cases, a Hayes EOS for the pure solid $\Psi_s(V, T)$ is adequate. This provides a thermodynamically consistent framework for the P - α model. For this form of EOS the volume fraction has a similar effect to an endothermic reaction in that the partial Hugoniot loci with fixed ϕ are shifted to the left in the (V, P) -plane with increasing ϕ . The equilibrium volume fraction can then be chosen to match the concavity of the principal Hugoniot locus. An example is presented for the polymer estane. A small porosity of only 1.4 percent is required to match the experimental concavity in the Hugoniot data. This type of EOS can also be used to obtain the so-called “universal” Hugoniot for liquids.

INTRODUCTION

The principal Hugoniot locus is often used as the reference curve for a Mie-Grüneisen equation of state (EOS). Measurements of the Hugoniot locus typical yield the shock velocity as a function of the particle velocity. A distinctive feature of a porous material is that its Hugoniot locus in the (particle velocity, shock velocity)-plane is concave down. This led to the development of the P - α model by Herrmann, Carrol and Holt (9, 4). The pressure for a porous material is taken to have the form¹

$$P(V, e) = \phi P_s(\phi V, e)$$

where P_s is the pressure of the pure solid, V is the specific volume of the porous material, e is the specific internal energy, and ϕ is the solid volume fraction. In addition, the equilibrium volume fraction is assumed to be a function of P_s , *i.e.*, $\phi = \phi_{eq}(P_s)$.

With a slight modification, we show that this model can be formulated in a thermodynamic con-

sistent manner. Our starting point is the free energy used in mixture theory for two-phase flow. This allows us to define the entropy η , and the equilibrium sound speed, $c^2 = -V^2 \partial P / \partial V|_\eta$. The single phase limit of the Baer-Nunziato (1) can be used to account for non-equilibrium compaction dynamics. In this model, the time evolution of the volume fraction is determined by a rate equation. The dominant effect is that a weak compaction wave is fully dispersed and has a well defined physically meaningful width. Moreover, the equilibrium acoustic wave speed corresponds to the sound speed of the equilibrium EOS.

In analogy with reactive flow, for the non-equilibrium EOS one can define the Hugoniot loci with a fixed value of ϕ . In the (V, P) -plane it can be shown that the partial Hugoniots shift to the left as ϕ increases. Thus, the manner in which ϕ enters the EOS has the same effect as an endothermic reaction. As a consequence, for the same pressure, the shock speed of a porous material is always less than that of the pure solid material.

The thermodynamic framework is very general and the same form of EOS can be applied to other materials which have a concave Hugoniot loci in the

¹ In the P - α model, $\alpha = 1/\phi$ is the distension.

(particle velocity, shock velocity)-plane. Two classes of materials with this behavior are polymers and liquids. For a polymer, the porosity $1 - \phi$ can be interpreted as the ‘free volume’ between polymer chains. In the liquid case, $1 - \phi$ results from the non-crystal packing of molecules. Thermodynamics does not depend on the micro-structure, though the value of the porosity parameter for different classes of materials is expected to be very different. A granular material may have a porosity as high as 40% while the equivalent parameter for a polymer may be only a few percent.

As an example of a polymer we consider estane, which is a major component in the binder for the explosive PBX-9501. We construct an EOS that is thermodynamically consistent and matches the principal Hugoniot locus for estane. Finally we note that the so-called ‘universal liquid’ EOS (16) can also be viewed as an EOS for a slightly porous material. For lack of space we leave the details as an exercise to the interested reader.

FREE ENERGY

It is convenient to define an equation of state in terms of the Helmholtz free energy. Our basic assumption is that the free energy of a porous material has the form

$$\Psi(V, T, \phi) = \Psi_s(V_s, T) + B(\phi) \quad (1)$$

where Ψ_s is the free energy for the pure solid, $V_s = \phi V$ is the solid specific volume, and $B(\phi)$ is a potential energy associated with compaction. In addition, we assume that B is convex, *i.e.*, $\frac{dB}{d\phi} \geq 0$ and $\frac{d^2B}{d\phi^2} > 0$. From standard thermodynamic relations, it follows that the entropy of the porous material

$$\eta(V, T, \phi) = -\partial_T \Psi = -\partial_T \Psi_s = \eta_s(V_s, T) \quad (2)$$

is the same as the entropy of the pure solid, the specific internal energy of the porous material

$$e = \Psi + T\eta = e_s(V_s, T) + B(\phi) \quad (3)$$

is the sum of the pure solid internal energy plus a compaction potential, and the pressure

$$P(V, e, \phi) = -\partial_V \Psi = \phi P_s(V_s, e_s) \quad (4)$$

has the same form as in the P - α model.

The equilibrium volume fraction is determined by minimizing the free energy. Setting $\partial_\phi \Psi|_{V,T} = 0$, we obtain $V_s P_s = \phi \frac{dB}{d\phi}$. Hence, $\phi = \phi_{eq}(V_s P_s)$. Alternatively, the equilibrium pressure is given by

$$P_s = \beta(\phi, V) = \frac{1}{V} \frac{dB}{d\phi} = \frac{\phi_{eq}^{-1}(\phi)}{V_s}. \quad (5)$$

For a granular material β is referred to as the configuration pressure. An equilibrium equation of state is defined by

$$P_{eq}(V, e) = \phi P_s(\phi V, e - B(\phi)) \quad (6)$$

where $\phi(V, e)$ is the solution to the equation

$$V P_s(\phi V, e - B(\phi)) = \frac{dB}{d\phi}(\phi). \quad (7)$$

The equilibrium EOS differs slightly from the standard P - α model in that the pressure has an additional dependence on ϕ through the compaction potential and ϕ_{eq} is a function of $V_s P_s$ instead of only P_s .

For granular materials, the equilibrium volume fraction can be inferred from quasi-static compression experiments, see for example (7). For other materials it can be characterized empirically. A useful simple form (3) is

$$\phi_{eq}(V_s P_s) = 1 - (1 - \phi_0) \exp\left[-\frac{V_s P_s - V_{s0} P_{s0}}{V_{s0} P_c}\right]. \quad (8)$$

Here P_c is a parameter with dimensions of pressure that characterizes the compaction behavior. The potential B can be determined from either ϕ_{eq} or β by integrating Eq. (5).

Porosity is significant only at pressures below the pure solid yield strength. Often this is referred to as the crush-up pressure. Typically, the yield strength is much less than the bulk modulus. In this region of phase space the variation of V_s is small but its effect on the pressure is much larger than the thermal contribution. Thus, in practice the modifications wouldn’t have much affect on a numerical calculation. However, as a consequence of these modifications

$$de = de_s + \frac{dB}{d\phi} d\phi = -P_{eq} dV + T d\eta. \quad (9)$$

Since the fundamental thermodynamic relation is satisfied, the equilibrium EOS is thermodynamically consistent.

NON-EQUILIBRIUM FLOW

Fluid flow is determined by the Euler equations

$$\partial_t \begin{pmatrix} \rho \\ \rho u \\ \rho E \end{pmatrix} + \partial_x \begin{pmatrix} \rho u \\ \rho u^2 + P \\ \rho u E + u P \end{pmatrix} = \vec{0} \quad (10)$$

where u is the particle velocity, $\rho = 1/V$ is the density, and $E = e + \frac{1}{2}u^2$. With Eqs. (4) and (3) for the pressure, $P(V, e, \phi)$, and a rate equation for the non-equilibrium compaction dynamics

$$\frac{d\phi}{dt} = (\partial_t + u\partial_x)\phi = \frac{\phi(1-\phi)}{\mu_c} (P_s - \beta) \quad (11)$$

where μ_c is a relaxation parameter with dimensions of viscosity, we have the single phase limit of the BN-model (1, 2). On a time scale long compared to the relaxation time, the flow reduces to the Euler equations with the equilibrium EOS, $P_{eq}(V, e)$.

The frozen sound speed of the non-equilibrium model is just the sound speed of the pure solid, $c_s^2 = \frac{\partial P_s}{\partial \rho_s}|_{\eta} = \frac{\partial P}{\partial \rho}|_{\eta, \phi}$. The equilibrium sound speed is determined from the equilibrium equation of state, Eqs. (6) and (7), $c_{eq}^2 = \frac{\partial P_{eq}}{\partial \rho}|_{\eta}$. It is given by (12)

$$\left(\frac{c_{eq}}{c_s}\right)^2 = 1 - \left(\frac{\gamma_s - 1}{\gamma_s}\right)^2 \frac{c_s^2}{c_s^2 + \phi^2 \frac{d^2}{d\phi^2} B} \quad (12)$$

where $\gamma_s = \rho_s c_s^2 / P_s$ is the adiabatic exponent of the solid. Provided that $\gamma_s > 1$ and B is convex, $c_s > c_{eq} > 0$. As is typical for a relaxation model the equilibrium sound speed is less than the frozen sound speed.

We note that the sound speed based on the standard P - α model, see (15, Appendix A), is not derived from a thermodynamically consistent EOS. The P - α model corresponds to dissipating the energy associated with the compaction potential. The non-equilibrium dynamics can be generalized to have this effect (8). However, the extra dissipation would cause acoustic waves to be damped.

Fully dispersed shocks occur when the shock speed is in the range $c_{eq} < u_s < c_s$. For these waves, compaction work is sufficient to provide the necessary shock dissipation. To leading order the dissipation in smooth regions can be represented by a nonlinear viscosity (12). With such a viscosity, the wave

profiles of weak compaction waves would be determined from the Euler equations with the equilibrium EOS.

Hugoniot locus

Assuming the ahead and behind shock states are in equilibrium, the Hugoniot locus of a porous material is determined by the Hugoniot equation, $e - e_0 = \frac{1}{2}(P + P_0)(V_0 - V)$, with the equilibrium EOS. To understand the properties of the Hugoniot locus it is convenient to employ Eq. (4) for the pressure with the volume fraction regarded as an independent variable. This enables an analysis quite similar to that used in the study of the reactive fluid equations but with the volume fraction playing the role of the reaction progress variable.

We consider the “partial” Hugoniot loci with a fixed value of the the volume fraction behind the wave, subject to the condition that $\phi > \phi_0$. Due to the manner in which ϕ enters the EOS, it can be shown that with increasing ϕ the partial Hugoniot loci shift to the left in the (V, P) -plane. For a reactive material such a shift in the Hugoniot loci is associated with an endothermic reaction. However, here the compressive behavior rather than the energetics dominates. Since the shock speed is determined by $(\rho_0 u_s)^2 = \frac{P - P_0}{V_0 - V}$, and the particle velocity by $u_p^2 = (P - P_0)(V_0 - V)$, it follows that at a fixed P or u_p the shock speed decreases with increasing ϕ . The effect is largest for u_s near c_{eq} and causes $u_s(u_p)$ to be a concave function.

For a granular material, the EOS of the pure solid is used as a starting point. The intersection of the measured Hugoniot locus with the computed partial Hugoniot loci in the (V, P) -plane determine $\phi_{eq}(VP)$. The potential B is determined by integrating Eq. (5). The complete EOS is then given from the free energy, Eq. (1), along with the equilibrium condition, Eq. (7).

ESTANE HUGONIOT

By way of illustration, we apply the procedure described in the preceding section to construct an empirical thermodynamically consistent EOS that

Table 1. Equation of state parameters for estane.

ρ_0	1.2	g/cm ³
K_{T0}	7.37	GPa
N	5.8	—
Γ_0	1.1	—
ϕ_0	0.986	—
P_c	0.1	GPa
C_V	0.001	(MJ/kg)/K

matches the principal Hugoniot locus of estane. It is convenient to use a Hayes EOS (5, 11, 14) for Ψ_s since the free energy has a simple analytic form. The Hayes EOS is based on the following assumptions: (i) the specific heat C_V is constant, (ii) the Grüneisen coefficient has the form Γ/V is constant, and (iii) the isothermal bulk modulus has the form $K_T = K_{T0}(V_0/V)^N$. In addition, we use Eq. (8) for ϕ_{eq} .

The parameters ϕ_0 and P_c were used to match the downward concave portion of $u_s(u_p)$ for low values of u_p . The linear behavior for larger u_p was fit with the parameters K_{T0} and N . In the range of the experimental data the Hugoniot locus is insensitive to the other parameters. A reasonable fit is obtained with the parameters in table 1. The data and the fit to the Hugoniot loci in the (u_p, u_s) -plane are shown in figure 1. It is noteworthy that the concavity at low u_p can be obtained with a porosity of only 1.4 percent.

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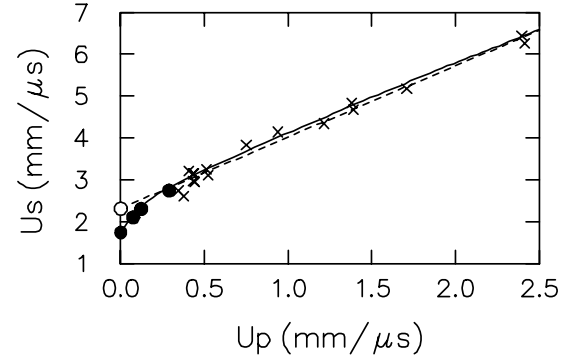


FIGURE 1. Estane Hugoniot locus. Data points are denoted by the symbol X, Marsh (13, p. 420), and by a solid circle, Dick (6, Fig. 30) or (10, Fig. 6). The solid line is the Hugoniot locus computed from the porous equilibrium equation of state. The dashed line is a linear fit to Marsh's data. The open circle is the intercept on the u_s axis of the linear fit.

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